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THE TECHNOLOGY OF AMMONIA PRODUCTION AT THE LEUNA WORKS

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In the synthesis of ammonia, a mixture of hydrogen and nitrogen is catalyzed under high pressure, part of the gases combining to form ammonia. The hydrogen is made from water gas, the nitrogen from generator gas. Both are produced by the gasification of solid fuels such as bituminous coke, or coke derived from the distillation of lignite, or from dried lignite.

Since the resumption of production at the Leuna Works in 1945, lignite coke has been used in production of the synthesis gas instead of bituminous coke, because the latter originates in the Western Zone and is now difficult to obtain. This has caused a change in the composition of the gases, which is shown in the following table:

Type of Gas	Composition in percent of volume						Grams of S per cum of N	
	H <sub>2</sub>	CO	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> S	Cum of N	per ton N
Bituminous Coke								
Water gas	49.0	38.0	6.0	6.3	0.5	0.2	3.0	2,862
Generator gas	5.0	30.0	57.0	7.0	6.5	0.3	4.3	1,343
Mixture 2.13:1	35.0	35.4	22.3	6.5		0.23	3.4	4,205
Lignite Distillation Coke								
Water gas	41.0	32.0	1.2	23.1	1.5	1.2	17.2	3,235
Generator gas	9.0	27.0	54.0	9.1	0.5	0.5	7.2	1,662
Mixture 1.95:1	30.2	30.3	19.1	18.3	1.2	0.97	13.9	4,897

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Water gas and generator gas are mixed in such a proportion that the gas mixture will supply, after further reaction and cleaning stages, a very pure mixture suitable for ammonia synthesis, consisting of about 75 percent hydrogen and 25 percent nitrogen. As the analysis shows, the gas mixture obtained from the lignite contains less hydrogen and less carbon monoxide, but more carbon dioxide and more methane, and a great deal more hydrogen sulfide than the gas obtained from bituminous coke. The high CO<sub>2</sub> content of the mixture is a disadvantage for the conversion of CO, because the carbon dioxide already present in the original gas requires an additional high excess of steam in this equilibrium reaction. The gases made from lignite also contain small amounts of compounds which form resins and other organic impurities. The amounts of these impurities are only a few milligrams per cubic meter of gas, but they are catalyst poisons and very difficult to remove completely.

The changes in composition of the gas have had an effect on the processing of the gas mixture. Because the content of hydrogen and carbon monoxide is now lower, the amount of crude gas required for the production of one ton of ammonia nitrogen is much greater than it was before, a fact which has, of course, affected the capacity of the plant very unfavorably.

Both components of the gas mixture are made by continuous gasification of lignite distillation coke in Winkler generators, at temperatures between 900 and 1000° C. The heat of the gas is used for steam generation in a heat exchanger.

The sulfur is then removed. Because the sulfur content is very high, this is done in two stages, a so-called "coarse sulfur removal" by means of the Alkazid process, and then a "fine sulfur removal" by means of active carbon. Application of both processes yields very pure elemental sulfur.

Most of the carbon monoxide is then removed by conversion. It is converted into carbon dioxide and hydrogen by means of steam at 450 to 500°C in presence of a catalyst. A remainder of 4 to 5 percent of carbon monoxide and 30 percent of carbon dioxide are left.

The first three stages of five-stage compressors then put the gas under a pressure of 26 to 27 atmospheres. After the third compression stage, it is washed with water to remove the carbon dioxide, leaving a residual content of 1 or 2 percent. The fourth and fifth stages then compress the gas to about 250 atmospheres.

The compressed mixture is washed with an ammoniacal copper solution and then washed a second time with an aqueous ammonia solution to remove the last residues of carbon monoxide and dioxide. The copper solution is regenerated and used again. The gas for the synthesis is finally cleaned catalytically to remove all impurities.

Some details on the individual stages of the process follow:

#### The Winkler Generator

Recently, an innovation has been introduced at Leuna, in the form of a Winkler generator which has no grate and no stirring arm. The cylindrical shaft is closed at the bottom by a slender cone. The material for gasification is injected into the shaft about 2 meters above the point of the cone by means of nozzles. Fuel feed is the same as in the old-type generators. The fuel parts are circulated much more efficiently than in the grate-type generators, forming a fountain which reaches half-way up the generator. The contact time is therefore longer. Furthermore, the new construction is slightly superior in respect to consumption figures and the quality of the gas, and it does

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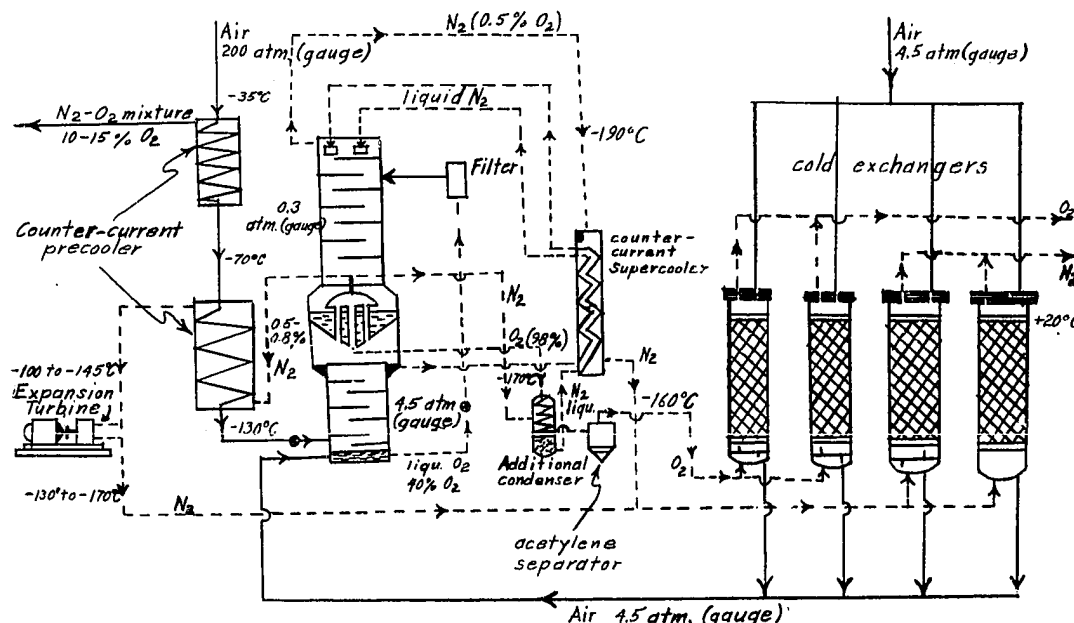
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away precisely with those parts which are most susceptible to breakdowns, namely the grate and the agitation mechanism. New Winkler generators, therefore, will be built only in this version.

### Oxygen and Nitrogen Production

The oxygen required for the production of water gas from lignite distillation coke is made by liquefaction and fractionation of air by the Linde-Fraenkl process. The process is shown in the schematic diagram below:



The process uses cold accumulators operating alternately in place of the tubular cold exchangers used previously. The cold exchangers are 4 to 5 meters high, about one meter in diameter, and contain a cold-storing mass of maximum surface. They are alternately charged with the air to be fractionated, and its fractionation products, nitrogen and oxygen. Valves operated by compressed air serve for regulating or reversing the direction of flow. These valves are attached to the top of the vessels. The bottom of the vessel is fitted with automatic check valves. Two accumulators each operate together, one pair serving for cold exchange between air and the oxygen which is produced, the other pair for cold exchange between air and nitrogen.

The cold-accumulators make pre-cleaning of the air which is to be fractionated unnecessary. Water vapor and carbon dioxide from the air condense on the cold hurdles during passage through the accumulator, and are carried off again when the accumulators are filled with oxygen and nitrogen.

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The reversal occurs every 3 minutes. The timing is arranged in such a manner that a reversal takes place every 90 seconds.

The refrigeration required for covering losses is provided by decompression of about 5 to 10 percent of the air, which is under a pressure of about 200 atmospheres, and by decompression of part of the gaseous nitrogen in a decompression turbine.

The Linde-Fraenkl process effects a great saving in energy and thus lowers the production costs of oxygen considerably. Originally, however, this process could produce, in addition to the 98 to 99 percent pure oxygen, only very impure nitrogen which contained 3 to 4 percent oxygen. Since pure nitrogen is needed at Leuna for scavenging and compression of high-pressure apparatus, especially in ammonia production, a number of small Linde apparatuses, operating on the old Linde process, had to be retained. They are much less economical, however, and the Leuna Works rebuilt the Linde-Fraenkl installations for the simultaneous production of pure nitrogen.

This modification, previously suggested for use in standard Linde apparatus by Lachmann, consists of the attachment of a gas tap in the middle of the upper portion of the column which removes a relatively small part of the oxygen-nitrogen mixture present at this point in the rectification column. The ratio of liquid to gas thus becomes greater above the tap, facilitating rectification in the upper portion of the column, so that both oxygen and nitrogen can be obtained in a very pure state. The amount of gas removed is about 5 or 6 percent of the total. Its low temperature is used for precooling of the high-pressure air in the counter-current precooler. The amount of air under high pressure to be used must be slightly increased to make up for refrigeration losses and in order to obtain the same quantities of oxygen as before. This additional quantity of air also supplies sufficient oxygen and nitrogen for removal of impurities from the cold accumulators. The energy consumption, however, is not higher than it is in apparatus which does not produce nitrogen because the total yield of oxygen is higher, and the specific energy consumption, i.e. the consumption of energy per equal quantity of 100 percent pure oxygen, has not increased. The new method thus not only eliminates the necessity of operating a special Linde apparatus for producing nitrogen, but is also more economical.

The Linde-Fraenkl apparatus, depending on its size, can supply 2500 to 3000 cubic meters of pure oxygen per hour, and 9000 to 12,000 cubic meters of nitrogen, which contain less than 0.5 percent oxygen, per hour.

The hurdles in the cold accumulators are made of ribbed aluminum ribbon 25 millimeters wide wound to form a flat disc. Lately, iron ribbons coated with an aluminum film to prevent corrosion have been used instead. While the specific heat of iron is lower than that of aluminum, the specific weight is higher and the heat capacity therefore almost as great.

#### Sulfur Removal and Carbon Monoxide Conversion

The removal of sulfur from the gas for synthesis used to be carried out exclusively with active carbon, since the gas produced from bituminous coke contains only 3 to 4 grams of sulfur per cubic meter in the form of hydrogen sulfide. The gas made from lignite coke, however, has a sulfur content of approximately 15 grams per cubic meter, and the active carbon process alone was not sufficient for removal. The so-called "alkazid" method, which is widely known and used, had to be introduced as a preliminary step to treatment with active carbon. It is based on the property of solutions of the alkali salts of weak organic acids to absorb hydrogen sulfide at normal temperatures and to release it again when heated. Salts like potassium aminopropionate

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are suitable for this purpose. The "Alkazid" liquids can be loaded with very large quantities of hydrogen sulfide, and then regenerate by simple steam heating. The sulfur yielded by this process is highly pure, containing only 0.02 to 0.03 percent moisture, catalyst dust, and bituminous impurities, and is light yellow in color.

The question of materials caused difficulties for years. All cold parts of the apparatus could usually be built of iron, but if hot liquids were used, the iron had to be protected by brickwork. For all apparatus transferring heat, aluminum could generally be used, but serious corrosion would occasionally appear, quite suddenly and often only after the part had been in operation for a long time. It was finally possible to eliminate these difficulties by careful analysis of the "Alkazid" liquid and by adding a carefully controlled amount of silicic acid in the form of water glass. V2A steel would be even better than aluminum, because it is absolutely corrosion proof against Alkazid.

The Alkazid process reduces the hydrogen sulfide content of the mixture gas to 3 or 4 grams per cubic meter.

The process is followed by the active carbon treatment. It consists of a catalytic oxidation of the hydrogen sulfide to elemental sulfur which is adsorbed in the pores of the active carbon. When the carbon is saturated, the sulfur is dissolved by ammonium sulfide solution, forming ammonium polysulfide. This is steam boiled under pressure, and pure, elemental sulfur is obtained. The vapors are cooled and condensed, and the ammonium sulfide solution is recovered. The carbon is cleaned with water and steam, and used again. Small quantities of ammonia in the gas expedite oxidation of the hydrogen sulfide.

The carbon monoxide in the gas from which the sulfur has been removed is converted by water vapor in the presence of a catalyst to carbon dioxide and hydrogen. The carbon monoxide thus serves for the production of hydrogen, however, for reasons of economy not all of it is converted, but 4 or 5 percent of the carbon monoxide remain, and are removed at a later stage by washing under pressure with copper solution. The catalyst is iron oxide, mixed with chromium oxide; the reaction takes place at temperatures between 400 and 500°C.

This stage of the production has been very badly affected by the conversion from bituminous to lignite coke. The high carbon dioxide content requires a high excess of steam for conversion of the carbon monoxide, because this is an equilibrium reaction; the results are higher steam losses and a greater steam consumption. The additional consumption of steam, in terms of ammonia produced, amounts to 50 percent or more.

#### Gas Compression

The compression of the converted gas takes place in five-stage piston compressors, driven partly by steam, partly by gas, and partly by electricity. The first three stages compress the gas to 26 or 27 atmospheres. It is washed under this pressure to remove the carbon dioxide, and then compressed to 250 atmospheres in the two last stages. Intermediate cooling is carried out after each stage. The condition of the cooling water is important, both for the life of the cooling tubes and for the efficiency of the operation. It has been found that the carbonate hardness can be as low as 3° at temperatures of 35 to 40°C, without any occurrence of corrosion but the water will cause neither corrosion nor sediments in the tubes if the carbonate hardness is between 7.2 to 7.4°. The longevity of the tubes is increased from 2 years to 6 to 8 years by formation of a protective film due to the use of water having an appropriate degree of hardness.

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Removal of Carbon Dioxide

The gas is washed under a pressure of 25 to 26 atmospheres to remove the carbon dioxide. Washing takes place in high cylindrical towers filled with earthenware rings. The water is supplied from the low-pressure water system of the plant, brought to the required pressure by centrifugal pumps, and pumped into the scrubbing towers which are connected in parallel.

The potential energy if the water, which is charged with carbon dioxide, is recovered and used for feeding water into the tower against the gas pressure. For that purpose it is decompressed to almost atmospheric pressure in Pelton turbines. The Pelton turbines are coupled with the centrifugal pumps, and about 50 or 55 percent of the total energy requirements for pressure water can be obtained by this method.

Instead of water under pressure, chemical absorption can be used for the removal of carbon dioxide at atmospheric pressure. This method has the advantage that the carbon dioxide to be removed does not have to be compressed to a pressure corresponding to that of the scrubbing water, so that considerable expense for the compression process is eliminated.

At Leuna, part of the converted gas is treated with ammonia for the removal of carbon dioxide. This yields ammonium carbonate, which is used for the manufacture of ammonium sulfate by double decomposition with either gypsum or anhydrite.

Both gases, one scrubbed with water under pressure, and the other treated with ammonia at normal pressure, are compressed separately to 250 atmospheres and then combined. The high-pressure lines behind the junction point showed bad corrosion effects which became more and more alarming. At the same time sediments of sludge were noticed. The substance responsible for the corrosion and sludge formation was hydrogen sulfide in the gas, present in a quantity of about 200 milligrams per cubic meter. Only after the hydrogen sulfide content had been reduced to less than 0.1 milligram per cubic meter was it possible to prevent corrosion and sludge formation almost completely. It was found that these corrosion effects in iron apparatus and pipelines will always occur whenever hydrogen sulfide, oxygen, and moisture are present at the same time. At Leuna, a check is made on corrosion by the insertion of test sections into susceptible high-pressure lines. The sections whose eight is known are periodically removed and weighed. Corrosion effects can be determined after an exposure as short as 2 or 4 weeks.

Copper Washing

The carbon monoxide and carbon dioxide still present in the gas must be removed. This is carried out by washing with an ammoniacal solution of copper carbonate under 240 to 250 atmospheres pressure. The copper solution is regenerated and used again.

The use of gases made from lignite created an unforeseen difficulty. The copper solution will occasionally foam while in the scrubbing towers. Part of the solution is carried out with the purified gas, thus reducing the degree of purity of the gas and the efficiency of the scrubbers. It is therefore necessary to prevent foam formation. At the beginning, small quantities of castor oil were added to the copper solution during the regeneration process. After the outbreak of the war castor oil became unobtainable, and an oil for corrosion prevention made by Rhenania of Hamburg was used instead, a machine oil containing a naphthene sulfonic acid as emulsifier. Since it could not be obtained in uniform quality, and therefore turned out to be unreliable, other means were tested for foam prevention. Of the many substances investigated, alcohols having more than 12 carbon atoms, preferably 15 or 16, or

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hydrocarbon mixtures of the synol synthesis with boiling points between 220 and 260°C were found to be the most effective. These anti-foaming agents are used in small quantities, only 1 or 2 liters per day for 500 cubic meters of copper solution.

#### Catalytic Gas Purification

This process serves to remove the last traces of impurities which might poison the catalyst, by turning the residua of carbon monoxide and dioxide into methane, and by eliminating the sulfur still present in the form of organic sulfur compounds.

Most other ammonia synthesis plants use a nickel catalyst. Since this catalyst is very sensitive to sulfur, it is preceded by a copper and iron catalyst. The temperature is 300 to 350°C, and the pressure is the same as that used in the synthesis stage.

Leuna employs a different system. The temperature is only 200 to 220°C, and the catalyst is the reduced catalyst of the ammonia synthesis. It consists mostly of pure iron, with small amounts of aluminum oxide and potassium oxide added because of their promotion effect. At a temperature of 200°C, when ammonia synthesis will not yet take place, this catalyst has a high purification effect and long life. The purification effect is lowered only at higher temperatures when the formation of ammonia begins to take place. This catalyst has an advantage over nickel, because the regeneration of an exhausted nickel catalyst is a laborious process, while the iron catalyst merely has to be melted down in the presence of oxygen and then reduced in order to be ready for use again.

The catalyst converts the carbon monoxide and dioxide and the unsaturated hydrocarbons still present into methane and ethane to the extent of 90 percent. The carbon dioxide content is reduced from 0.03 percent to 0.003-0.005 percent.

#### The Ammonia Synthesis

The most important part of the synthesis apparatus is, of course, the catalyst furnace which has undergone a number of changes and improvements. Most of these changes were made on the interior equipment of the furnace. The Leuna furnaces are built on the tube principle. The catalyst tubes form a bundle, with the tubes touching each other. Space is well utilized. The preheated gas flows past these tubes, entering the space at the tapered end of the tubes, then flows upward, and back down through the catalyst tubes. The high velocity of the flow effects good heat transfer and high efficiency. At a pressure of 230 atmospheres, 10 percent by volume of the gas leaving the furnace has been converted to ammonia, or 20 percent of a quantity of gas is turned into ammonia during one passage of the gas through the furnace. Because of this high efficiency, each Leuna catalyst furnace can produce 30 to 35 tons of nitrogen in the form of ammonia per day.

#### Removal of Foreign Gases From the Gas Cycle

Despite the catalytic purification, the gas does not consist only of pure hydrogen and nitrogen. The other components methane and argon, are not catalyst poisons, but simply do not take part in the reaction. The percentages are about 1.3 percent methane and 0.3 to 0.4 percent argon.

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Removal would be a difficult and expensive job, and therefore is not carried out. The two gases are carried along into the gas cycle. To prevent them from accumulating there and thereby impairing the efficiency of the ammonia catalyst furnaces, part of the gas in the cycle is always decompressed, in such quantities that the content of foreign gas remains low. If the content of foreign gas is high, this also means high losses of hydrogen and reduced efficiency. This was prevented at Leuna by a special method of arranging the gas intake and exhaust. This innovation did not require any new apparatus, it consisted merely in a change of the intake and exhaust controls of the cycle.

The entire cycle arrangement consists of the catalyst furnaces and their auxiliary equipment in parallel arrangement, and the circulation pumps, also in parallel arrangement. Furnaces and pumps are connected by joint high-pressure lines. The incoming gas used to be distributed to all furnaces, and the removal of foreign gases by decompression of part of the gas also took place as evenly as possible at several points. The entire apparatus was a uniform cycle, with the gas having the same composition at all furnace points. Now, however, the incoming gas is supplied only to a part of the furnace battery, about the first third. The gas to be exhausted from the cycle is decompressed at the other end. Thus, the gas of the cycle moves to the end of the furnace battery, and the content of foreign gases increases toward that direction. Since only that part is decompressed, the foreign gases are removed from there as a highly concentrated mixture. This is easily explained by the fact that the quantity of synthesis gas becomes smaller and smaller as it goes from one oven to the next, while the quantity of the foreign gases which take no part in the reaction remains constant, until it is removed at the end point of the cycle.

Only in the final stage is there any effect on the efficiency of the catalyst furnaces. However, this final stage consists of only two furnaces out of a total of more than 20, so that the loss of efficiency, as far as the entire plant is concerned, is very slight.

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